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TRANSACTIONS

Biochemistry of Filamentous Fungi. VII.

Mycelial Constituents of Oospora sulphurea-ochracea. Part IV. On the Constitution of Osoic Acid and its Derivatives.

By Hidejiro NISHIKAWA.

(Tottori Agricultural College)

Received December 8, 1941.

Further investigations on the constituents of *Oospora sulphurea-ochracea* have to some extent elucidated the constitution and interrelation of three of them (A, D and F) which will be described in the present communication.

A, D and F differ only in the number of methyl groups they contain; they are di-, tri- and monomethyl derivatives respectively of a methyl-free compound for which the name, osoic acid, is proposed for brevity (in Part II(1) it was provisionally labelled F′).

Osoic acid $C_{15}H_{12}O_8^*$ was formed from either A or F through potash fusion and an expanded formula $C_{13}H_7O\cdot(OH)_3(COOH)_2$ has now been assigned to it. The formula was deduced from the following observations:

(1) Diazomethane readily introduces into D or A one or two more methyl groups respectively, giving tetramethylosoic acid I. (For tetramethylosoic acid II *v. infra.*)

(2) By means of prolonged action of a large excess of diazomethane an additional methyl group can be introduced into the above tetramethylosoic acid I, perfectly neutral pentamethylosoic acid now being formed.

(3) By the action of methyl alcoholic potash upon tetramethylosoic acid I two methyl groups are removed from it, giving a dimethyl derivative, which will be called dimethylosoic acid II as against its isomer A, dimethylosoic acid I.

(4) Similarly methyl alcoholic potash deprives pentamethylosoic acid of two methyl groups out of five. A trimethyl derivative thus formed, to which the name trimethylosoic acid II is given as against its isomer D, trimethylosoic acid I, is revealed by titration to be dibasic. As the original pentamethylosoic acid is perfectly neutral, the detached groups are supposed to be combined as methyl ester, whereas the remaining three must be linked as methyl ether.

(5) Equally dimethylosoic acid II must have two free carboxyl groups. Its

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* In Part II the molecular formula of osoic acid was erroneously given which is now corrected.

isomer, dimethylosoic acid I, as it is soluble in bicarbonate solution, must have one free carboxyl group. Methyl groups are supposed to occupy the other carboxyl group and one of hydroxyl groups.

(6) As D, trimethylosoic acid I, is insoluble in bicarbonate solution, it will contain no free carboxyl group, two of its three methyl groups being employed for esterification and the remaining one combined as ether.

(7) The action of methyl alcoholic potash upon trimethylosoic acid I eliminates two methyl groups and converts it into F, monomethylosoic acid, the fact being in accord with the inference in (6).

(8) Dimethylosoic acid I loses one of methyl groups by the action of methyl alcoholic potash and is converted into F, this being obviously hydrolysis of ester. From these facts dimethylosoic acid I is a monomethyl ether monomethyl ester of osoic acid.

(9) One methyl group remaining in monomethylosoic acid is doubtlessly combined as ether, which is eliminated only when potash fusion is applied.

Piecing together these deductions the compounds mentioned above will be represented by the summarized formula below:

$$C_{13}H_7O \left\{ \begin{array}{l} COOR_1 \\ COOR_2 \\ OR_3 \\ OR_4 \\ OR_5 \end{array} \right.$$

	R_1	R_2	R_3	R_4	R_5
Pentamethylosoic acid	Me	Me	Me	Me	Me
Tetramethylosoic acid I	Me	Me	Me	Me	H
Tetramethylosoic acid II *	H	Me	Me	Me	Me
Trimethylosoic acid I	Me	Me	Me	H	H
Trimethylosoic acid II	H	H	Me	Me	Me
Dimethylosoic acid I	H	Me	Me	H	H
Dimethylosoic acid II	H	H	Me	Me	H
Monomethylosoic acid	H	H	Me	H	H
Osoic acid	H	H	H	H	H

Though there is some uncertainty except in the first and the last compounds as to which functional group or groups are involved in methylation, seven out of eight oxygen atoms in osoic acid are thus characterized, the function of the remaining one being yet to be determined. The proportions of carbon and hydrogen in osoic acid suggest the presence of two benzene rings and the linkage of diphenyl ether through the unconfirmed oxygen atom will be one of plausible structures. Attempts to grasp the nucleus, however, have so far been without success.

Ferric chloride reaction of osoic acid and its derivatives in alcoholic solution is shown in Table I.

TABLE I.

Pentamethylosoic acid	*nil*
Tetramethylosoic acid I	violet, gradually changing to pale brown
Tetramethylosoic acid II *	*nil*

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* v. infra.

Trimethylosoic acid I	violet, gradually changing to pale brown
Trimethylosoic acid II	*nil*
Dimethylosoic acid I	deep violet
Dimethylosoic acid II	reddish violet, slowly fading
Monomethylosoic acid	deep violet
Osoic acid	deep violet

From the above table it may be inferred that the free hydroxyl group which resists methylation is responsible for fading violet reaction, while one of the other two hydroxyl groups accounts for deep violet coloration suggestive of that of salicylic acid. The presence of a carboxyl group in the *ortho*-position of it might be anticipated.

ACTION OF CONC. SULPHURIC ACID UPON OSOIC ACID AND ITS DERIVATIVES.

Concentrated sulphuric acid deprives osoic acid of one molecule of water, giving anhydroosoic acid, which on methylation by means of diazomethane takes up four methyl groups and gives rise to a neutral tetramethyl derivative of anhydroosoic acid. On treatment of this neutral compound with alcoholic potash it loses one methyl group and is converted into a monobasic acid which is identical with the dehydration product of trimethylosoic acid II by conc. sulphuric acid. From these observations it will be considered probable that the dehydration in osoic acid took place between a carboxyl group of one benzene ring and a hydrogen of the other, closure to a xanthone nucleus being a probable supposition. If this be the case, the molecular dimension of this compound is just one oxygen atom more than the xanthone derivative, 3-methyl-1 : 6-dihydroxy-8-carboxyxanthone, obtained from sulochrin(2). Zinc dust distillation or fusion, however, has not so far given any clue to the existence of xanthone ring in this compound. Nor has potash fusion given any fragments suggestive of its structure. Anhydroosoic acid forms beautiful crystals from pyridine with two molecules of solvent of crystallization.

On similar treatment of monomethylosoic acid with conc. sulphuric acid a corresponding dehydration product is formed which, when recrystallized from pyridine, comes out in beautiful crystals with one molecule of pyridine of crystallization. In the case of dimethylosoic acid I simultaneous dehydration and demethylation seem to occur and the resulting substance is nothing but the anhydromonomethylosoic acid just mentioned above.

Anhydroosoic acid and anhydromonomethylosoic acid in alcoholic solution give a wine-red coloration with ferric chloride which is in marked contrast with a violet coloration in osoic acid, monomethylosoic acid, etc.

Action of conc. sulphuric acid in the cold upon pentamethylosoic acid does not effect dehydration but gives rise to a substance one methyl less than the original substance. This is an isomer of tetramethylosoic acid I and will be called tetramethylosoic acid II. The reaction may be explained as follows. Of two carboxyl groups the one which is concerned in ring-closure on sulphuric acid treatment of osoic acid and monomethylosoic acid is here esterified and consequently hindered from being involvod in dehydration. Conc. sulphuric acid effects only to drop a methyl group off the second carboxyl group situated at a remoter position. Upon trimethylosoic acid II on the other hand conc. sulphuric acid can effect dehydration as the carboxyl groups in this compound are considered to be both methyl-free due to hydrolysis. That anhydrotrimethylosoic acid II thus formed has the same nuclear system as anhydroosoic acid is obvious from the fact that on methylation the former is converted into the fully methylated product of anhydroosoic acid and conversely on treatment with ethyl alcoholic potash for some hours tetramethylanhydroosoic acid gives rise to anhydrotrimethylosoic acid II.

The mutual relations of osoic acid and its derivatives mentioned above will be as shown in the following scheme:

EXPERIMENTAL.

Dimethylosoic acid I.

M.p. 214°. Optical inactivity and other properties have been recorded in the previous paper(1). Methoxyl content freshly estimated showed correct value (Found: 17.37%. $2CH_3O$ in $C_{17}H_{16}O_8$ requires 17.82%).

Osoic acid.

Produced through potash fusion from either dimethylosoic acid I or monomethylosoic acid as described in the previous communication(1). Other methyl derivatives of osoic acid, *e.g.* tetramethylosoic acid I, give it as well on potash fusion. There the formula $C_{15}H_{14}O_8$ was given to it based on high H values, which, it is now evident, were due to its being exceedingly hygroscopic. Even kept in a desiccator it increases in weight. A fresh analysis with a carefully dried specimen gave the right value (Found: C, 55.90; H, 4.03%. $C_{15}H_{12}O_8$ requires C, 56.25; H, 3.76%).

Tetramethylosoic acid I.

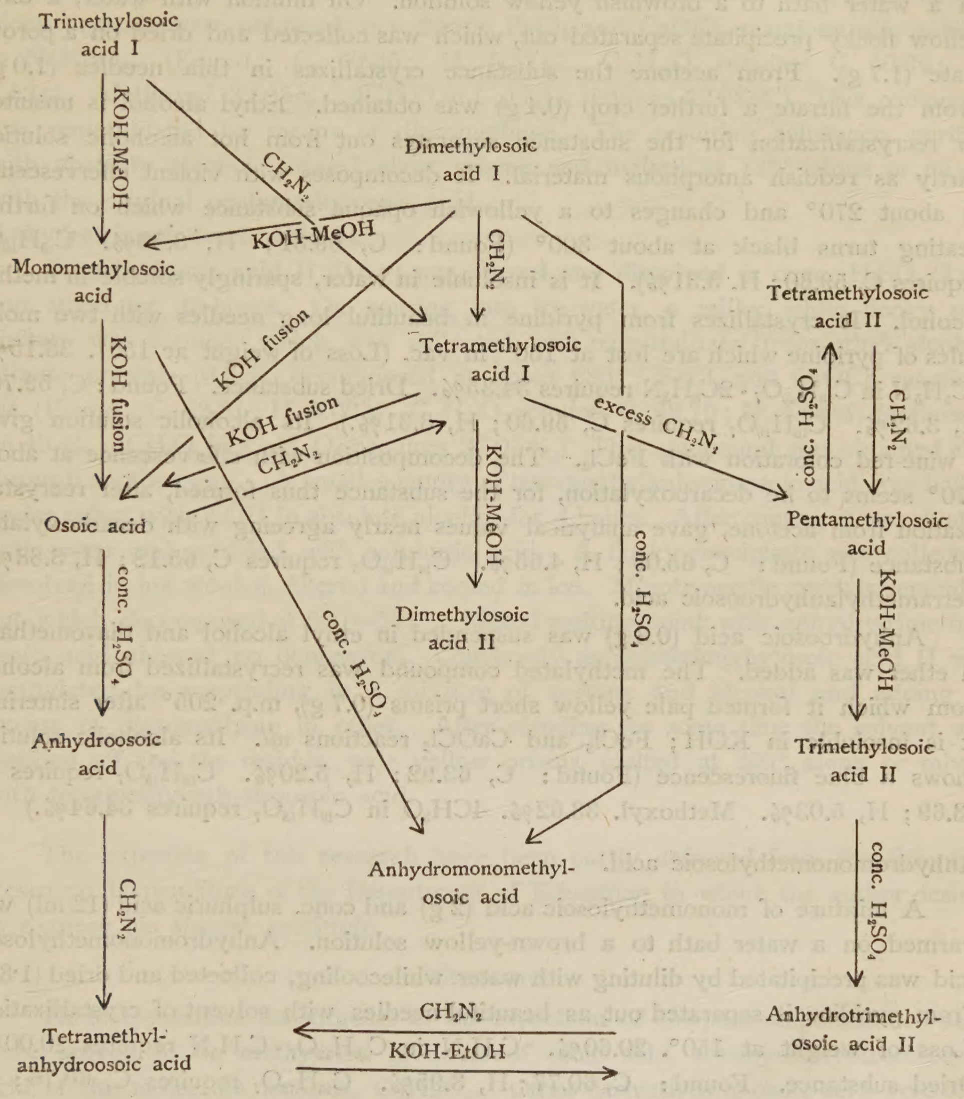
To dimethylosoic acid I (4.8 g) dissolved in alcohol was added an ethereal solution of diazomethane. The solvent was then distilled off and the residue was recrystallized from alcohol. Platelets (2.4 g), m.p. 129°. It was also produced from trimethylosoic acid I in a similar manner. Sometimes crystals of lower m.p. were obtained which were found to be due to contamination of pentamethylosoic acid (Found: C, 60.52; H, 5.07%. $C_{19}H_{20}O_8$ requires C, 60.64: H, 5.32%. Methoxyl. 32.30, 32.89%. $4CH_3O$ in $C_{19}H_{20}O_8$ requires 32.98%).

Dimethylosoic acid II.

Tetramethylosoic acid I (1 g) was boiled under reflux with methyl alcoholic potash (3 g KOH in 30 ml MeOH) for an hour. On cooling the solution was acidified and the separated solids were collected (0.8 g). The substance, on recrystallization from alcohol, formed thin prisms, m.p. 240° (decomp.). (Found: C, 58.49; H, 4.76%. $C_{17}H_{16}O_8$ requires C, 58.62; H, 4.60%. Methoxyl. 17.89%. $2CH_3O$ in $C_{17}H_{16}O_8$ requires 17.82%.)

Pentamethylosoic acid.

To tetramethylosoic acid I (5 g) dissolved in a small quantity (20 ml) of acetone a large excess of diazomethane in ether (prepared from 14.3 g of nitrosomethylurea) was added. The mixture was kept in a stoppered vessel for a week. Crystals deposited gradually on the wall and bottom of the vessel, which were collected (3.2g). It crystallizes in platelets from methyl alcohol, m.p. 149°. (Found: C, 61.34; H, 5.65%. $C_{20}H_{22}O_8$ requires C, 61.54: H, 5.64%. Methoxyl. 38.38, 38.28%. $5CH_3O$ in $C_{20}H_{22}O_8$ requires 39.74,)



Trimethylosoic acid II.

Pentamethylosoic acid (1 g) was boiled with KOH (5g) in methyl alcohol under reflux for a few hours. The solution was cooled and acidified and the separated solids were recrystallized from methyl alcohol, yield almost quantitative. Thick block crystals, m.p. 211°. (Found: C, 59.27; H, 5.03%. $C_{18}H_{18}O_8$ requires C, 59.67; H, 4.97%. Methoxyl. 25.21%. $3CH_3O$ in $C_{18}H_{18}O_8$ requires 25.69% Mol. wt. by titration as a dibasic acid. 373.9. $C_{18}H_{18}O_8$ requires 362.)

Anhydroosoic acid.

A mixture of osoic acid (2 g) and conc. sulphuric acid (12 ml) was warmed on a water bath to a brownish yellow solution. On dilution with water, a dirty yellow flocky precipitate separated out, which was collected and dried on a porous plate (1.7 g). From acetone the substance crystallizes in thin needles (1.0 g). From the filtrate a further crop (0.4 g) was obtained. Ethyl alcohol is unsuited for recrystallization for the substance separates out from hot alcoholic solution partly as reddish amorphous material. It decomposes with violent effervescence at about 270° and changes to a yellowish opaque substance which on further heating turns black at about 300° (Found: C, 59.31; H, 3.53%. $C_{15}H_{10}O_7$ requires C, 59.60; H. 3.31%). It is insoluble in water, sparingly soluble in methyl alcohol. It crystallizes from pyridine in beautiful long needles with two molecules of pyridine which are lost at 150° in vac. (Loss of weight at 150°. 33.15%. $2C_5H_5N$ in $C_{15}H_{10}O_7 \cdot 2C_5H_5N$ requires 34.35%. Dried substance. Found: C, 59.70; H, 3.62%. $C_{15}H_{10}O_7$ requires C, 59.60; H, 3.31%.) Its alcoholic solution gives a wine-red coloration with $FeCl_3$. The decomposition with effervescence at about 270° seems to be decarboxylation, for the substance thus formed, after recrystallization from acetone, gave analytical values nearly agreeing with decarboxylated substance (Found: C, 65.09; H, 4.65%. $C_{14}H_{10}O_5$ requires C, 65.12; H, 3.88%).

Tetramethylanhydroosoic acid.

Anhydroosoic acid (0.8 g) was suspended in ethyl alcohol and diazomethane in ether was added. The methylated compound was recrystallized from alcohol, from which it formed pale yellow short prisms (0.7 g), m.p. 205° after sintering. It is insoluble in KOH; $FeCl_3$ and $CaOCl_2$ reactions *nil*. Its alcoholic solution shows a blue fluorescence (Found: C, 63.92; H, 5.20%. $C_{19}H_{18}O_7$ requires C, 63.69; H, 5.03%. Methoxyl. 33.62%. $4CH_3O$ in $C_{19}H_{18}O_7$ requires 34.64%.)

Anhydromonomethylosoic acid.

A mixture of monomethylosoic acid (2 g) and conc. sulphuric acid (12 ml) was warmed on a water bath to a brown-yellow solution. Anhydromonomethylosoic acid was precipitated by diluting with water whilecooling, collected and dried (1·8 g) From pyridine it separated out as beautiful needles with solvent of crystallization. (Loss of weight at 150°. 20.60%. C_5H_5N in $C_{16}H_{12}O_7 \cdot C_5H_5N$ requires 20.00%. Dried substance. Found: C, 60.77; H, 3.95%. $C_{16}H_{12}O_7$ requires C, 60.76; H, 3.80%. Methoxyl. 9.89%. CH_3O in $C_{16}H_{12}O_7$ requires 9.81%.) It changes colour at about 295° and decomposes completely over 340°. It is sparingly soluble in ethyl alcohol and gives a wine-red coloration with $FeCl_3$. Dimethylosoic acid I was treated with conc. H_2SO_4 in a similar manner. The resulting substance gave identical analytical figures with those of anhydromonomethylosoic acid. One of the methyl groups was dropped along with a molecule of water. (Loss of weight at 150°. 20.63%. Dried substance. Found: C, 60.84; H, 3.90%. Methoxyl. 9.31%.)

Tetramethylosoic acid II.

Conc. sulphuric acid (6 ml) was added to pentamethylosoic acid (1 g), the mixture was rubbed with a glass rod to a solution and stood overnight in a desiccator. The dark red solution was poured into ice-water. The yellow precipitate (0.9 g) was dissolved in hot alcohol (20 ml) and filtered. On cooling minute block crystals were obtained, m.p. 225° ; $FeCl_3$ and $CaOCl_2$ reactions *nil*; soluble in $NaHSO_3$. (Found: C, 60.35; H, 5.57%. $C_{19}H_{20}O_8$ requires C, 60.64; H, 5.52%. Methoxyl. 32.25%. $4CH_3O$ in $C_{19}H_{20}O_8$ requires 32.98%.) This compound was remethylated by means of diazomethane. The resulting substance, purified with absolute alcohol, formed short prisms and melted at 149° alone or mixed with the original pentamethylosoic acid.

Anhydrotrimethylosoic acid II.

Trimethylosoic acid II (0.5 g) was stirred and dissolved in conc. H_2SO_4 (4 ml) and stood for 45 hours. On pouring into ice-water, a milky white flocky precipitate was formed, which was collected and recrystallized from ethyl alcohol. Minute crystals (0.2 g), decomposed at about 280° ; $FeCl_3$ and $CaOCl_2$ reactions *nil*. (Found: C, 62.81; H, 5.02%. $C_{18}H_{16}O_7$ requires C, 62.79; H, 4.65%. Methoxyl. 26.40 %, $3CH_3O$ in $C_{18}H_{16}O_7$ requires 27.03%.) This compound was obtained also through another way. A small quantity of tetramethylanhydroosoic acid was boiled under reflux with KOH in absolute alcohol for 4 hours. After cooling it was diluted with water and acidified with sulphuric acid. A flocky precipitate was collected, dissolved in hot alcohol, filtered and cooled in ice. Minute needle crystals separated out which decomposed at 280~281°. Mixed melting point with anhydrotrimethylosoic acid showed no depression. Conversely anhydrotrimethylosoic acid II was methylated by suspending in a mixture of acetone and alcohol and adding an excess of diazomethane in ether. After standing for some time the solvent was distilled off and the residue, pale yellow prisms, melted at 205° alone or mixed with tetramethylanhydroosoic acid.

The expenses of this research have been partly defrayed from the Scientific Research Expenditure of the Department of Education to which the author desires to express his sincere gratitude.

SUMMARY.

Three crystalline constituents of the mycelium of Oospora sulphurea-ochracea were proved to be methylated products of osoic acid, a trihydroxydicarboxylic acid of the molecular formula, $C_{15}H_{10}O_8$. Other derivatives of osoic acid were also prepared.

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(1) Nishikawa, Bull. Agr. Chem. Soc. Jap., **13**, **1** (1937).
(2) Nishikawa, Acta Phytochim., **11**, 167 (1939).

ABSTRACTS
from
TRANSACTIONS published in JAPANESE

(Pages refer to the Japanese originals of this volume unless otherwise noted.)

Über die quantitative Bestimmung der Pyrethrine.

XI. Mitteilung. Über den Pyrethringehalt des Rauchs von Moskitostäbchen.*

(SS. 229～236)

Von Kiyosi Wakazono, Keizo Hiraoka, und Sankiti Takei.

(Aus d. Institut f. Chem. Forschung, Universität Kyoto;
Eingegangen am 4. 12. 1941.)

Es interessierte uns zu wissen, ob der wirksame Bestandteil im Rauch der Moskitostäbchen durch die unzersetzten Pyrethrine gebildet wird, da diese, wie bekannt, gegen Hitze sehr unbeständig sind. Es ist aber nicht unmöglich, daß bei dem Abbrennen der Rauchstäbchen die Pyrethrine im rotglühenden Punkt vollkommen zerstört werden, wogegen am gerade benachbarten Stäbchenteil eine gemässigte Temperatur zu erwarten ist, so daß von diesem Teil aus die unzersetzten Pyrethrine selbst zusammen mit den übrigen Gasbestandteilen in die Luft vergast werden. Von dieser Überlegung ausgehend haben wir versucht, aus dem von den Moskitostäbchen aufsteigenden Rauch die Pyrethrine in irgendeiner Form zu erfaßen.

Zunächst haben wir den aus den spontan verbrennden Stäbchen gebildeten Rauch mit dem Luftstrom in eisgekühlte Sauggefässe geleitet, von denen dann nach dem völligen Abbrennen das an den Wänden kondensierte Teermaterial mit Äther und Natronlauge abgespült wurde. Die Ätherauszüge wurden mit verd. Natronlauge und verd. Schwefelsäure nachgewaschen. Aus dem so behandelten neutralen Teerbestandteil konnten wirmittels unserer massanalytischen Methode 5～7% des in den abgebrannten Stäbchen enthaltenen Gesamtpyrethrins nachweisen. Weiter noch wurden aus der Ablauge von mehreren Analysen Chrysanthemum-monocarbonsäure (Amid, Schmp. 131°; Anilid, Schmp. 100～101°) und -dicarbonsäure (Schmp. 164°) identifiziert.

Auf Grund dieser Ergebnisse möchten wir annehmen, daß die Wirkung des von den Moskitostäbcheten verbreiteten Rauchs auf die Insekten zweifellos der Wirksamkeit der feinverteilten Pyrethrine zuzuschreiben ist und daß, da die Menge desselben verhältnismässig immer nur sehr gering sein dürfte, die Wirkung des Pyrethrins in dieser Form eben höchst effektiv sein muß.

* Moskitostäbchen: Aus pyrethrinhaltigem Insektenpulver in Stäbchenform hergestelltes Begasungsmaterial.

On the Alluvial Soil in Kakuritu Prefecture, Northeast Manchuria.

(pp. 237∼241)

By R. Kawashima, M. Nagata, S. Tanaka, and G. Tōyama.

(Agr. Chem. Laboratory, Kyûshû Imp. University; Received December 24, 1941.)

On a Slightly Podzolized and Regenerated Brown Forest Soil in Banseki Prefecture, Central Manchuria.

(pp. 242∼244)

By R. Kawashima, M. Nagata, S. Tanaka and G. Tōyama.

(Agr. Chem. Laboratory, Kyushu Imp. University; Received January 6, 1942.)

Der bakterielle Abbau der Aminosäuren. I. Mitteilung.

Der oxydative Abbau der Aminosäuren durch
Bac. proteus vulgavis Hauser.

(SS. 245∼256)

By Teijirô Uyemura.

(Wissenschaftl. Laboratorium von Ch. Takeda & Co. Ltd., Osaka;
Eingegangen am 26. 11. 1941.)

Study on Alcoholysis.

I. The Variation of Reaction Velocity to
the Kinds of Alcohol.

(pp. 257∼264)

By Hogai Ka and Kozo Kawakami.

(The Institute of Scientific Research Manchoukuo; Received November 28, 1941.)

Last year one of the authors reported a new method for the quantitative determination of glycerine even in the presence of other alcohols or impurities.

In the present method the alcoholysis of different kinds of alcohols, using $N/10$ NaOH as catalyser, was studied by determining the quantity of free glycerine in reaction mixture at definite intervals.

The alcoholysis was carried out by adding 100 cc of $N/10$ NaOH alcoholic solution to 50 gr of olive oil with constant stirring at 22∼24°C and the reaction fatty acid present was instantly combined with the alcohol to form the ester. was allowed to proceed for 24 hrs. The acetyl value and acid value were also determined during the course of the reaction. The following results were obtained :—

1. The acetyl value increased greatly at the first 10 minutes and then decreased later to a constant.

2. The acid value increased also as the reaction proceeded, but the quantity of the free fatty acid present was found to be less than that calculated from the increases of the acetyl value. Therefore, it may be considered that the excess of

fatty acid present was instantly combined with the alcohol to from the ester. So, in the so-called alcoholysis reaction the production of ester can be considered in two directions. One is the direct substitution of glycerine and alcohol, and the other the esterification of fatty acid delivered by the increase of acetyl value.

3. The quantity of ester production, both in the case of direct substitution and total ester production, the replacing power of the alcohols with odd number of carbon atoms was stronger than their respective adjacent member with even number of carbon atoms.

4. The replacing power was strongest with alcohols containing less than 5 carbon atoms, and decreased as the number of carbon atoms increased over six.

5. The replacing power of the secondary alcohols such as *i*-propyl alcohol was weakest among the alcohols, and for alcohols, which contain a ring such as benzyl alcohol the replacing power was also weak.

6. The replacing power of the normal alcohol was better than that of the *iso*-alcohol with the same number of carbon atoms.

From the above results it was found that the alcohols have a specific replacing power and it may be suggested that they may show a selective replacing power in alcoholysis.

Über die Vitamin-B_1 Adsorption durch Hefe.

(SS. 265~268)

Von M. ODA und K. NAGAO.

(Laboratorium von Meiji-Seito & Co. Ltd., Tokio. Eingegangen am 24. 12. 1941.)

On the Stimulant for Cane Sugar Formation in Plants. (X).

(pp. 269~272)

By Tetutaro TADOKORO and Takeshi SASAKI.

(Hokkaido Imperial University; Received December 1, 1942.)

On the Biochemical Properties of Tomato and Potato Virus. (3).

(pp. 273~275)

By T. TADOKORO, T. SAITO, and N. TAKASUGI.

(Hokkaido Imperial Tniversity; Received December 17, 1941,)

A New Simple Method for the Quantitative Determination of Glycerine (Supplement).

(pp. 276~278)

By Hogai KA.

(The Institute of Scientific Research, Manchoukuo; Received November 28, 1941.)

Further investigation on the method for the quantitative determination of glycerine based on Denigés glycerine and codein colour reaction was carried out. In this paper, ways were described for carrying out this method and the original equation (A) for the calculation of the percentage of glycerine was modified as follows :—

$$\text{Glycerine } \% = 0.0526 \times \text{Blue value} + 0.015 \quad \text{(A)}$$

Studies on Methionine and its Derivatives. (IV).

Nutritional Effect of $l(-)$-Methionine and its Derivatives for the Albino Rat on Cystine-Deficient Diet, especially that of the Oxydative Derivatives Containing Sulfur such as $l(+)$-Methionine Sulfoxide and $l(+)$-Methionine Sulfone.

(pp. 279～288)

By Yoshio Tsuchiya.

(S. Suzuki & Co. Ltd; Received December 24, 1941.)

In the present paper, the author has studied the replaceability of methionine with its derivatives in the cystine-deficient diet of albino rats, especially the oxydative derivatives containing sulfur such as methionine sulfoxide and methionine sulfone (a new amino acid).

And the relation between methionine and its oxydative derivativs and the mechanism of the transformation of methionine to cystine were discussed in some respects. The results obtained are summarized as follows:

(1) $l(-)$-Methionine showed a marked growth promoting effect on the rat on the cystine deficient diet.

(2) $l(+)$-Methionine sulfoxide showed the same effect as methione.

(3) The assumption is proposed that the effectiveness of $l(+)$-methionine sulfoxide is perhaps due to the return to methionine by some reducing agents such as cysteine, reduced glutathione, or, possibly, by some reducing enzymes. Methionine sulfoxide is reduced readily by hydriodic acid or slowly by cysteine. Accordingly, the oxidation of the sulfur contained in methionine does not occur *in vivo*. In other words, methionine sulfoxide is not formed as the intermediate in the transformation of methionine to cystine.

(4) The growth curves of rats fed with $l(-)$-methionine, $l(+)$-methionine sulfoxide, and $l(-)$-cystine were identical. It may be stated that the physiological availability of these compounds is the same.

(5) $l(+)$-Methionine sulfone had no nutritional effect. It is now assumed that neither the oxidation of the sulfur contained in methionine to sulfone stage in the course of the transformation of methionine to cystine, nor the reduction of this compound to methionine or methionine sulfoxide take place *in vivo*.

The latter fact was chemically demonstrated, i. e., methionine sulfone is not reduced either by hydriodic acid or by cysteine.

(6) γ-Methylmercapto-propyl-amine was not effective as cystamine, and rather toxic to some rats, causing retardation of the increase of the body weight, falling of hair, or death.

On Some Properties of the Cane Molasses Produced by the Sulphitation Process.

(pp. 289～296)

By Yoshi Iwata, Shinichi Suzuki, and Yutaka Kawai.

(Government Sugar Experiment Station, Tainan, Taiwan, Japan;
Received December 29, 1941.)

Studien über Denaturierung des Sericin (Seidenleime).

V. Mitteilung.

(SS. 297～307)

Von Z. Hirose.

(Aus dem Chemischen Institut für Seidenbau, der Aktiengesellschaft Gunze
Seisi zu Ayabe, Kioto-hu. Eingegangen am 3. 12. 1941.)

Studies on Arginase. (IV).

On the Purification of Beef Liver Arginase and Some Properties of the Purified Arginase.

(pp. 308～314)

By Matsunosuke Kitagawa and Masaharu Sirakawa.

(Institute of Agricultural Chemistry, Faculty of Agriculture, Kyushu Imperial
University, Fukuoka; Received December 24, 1941.)

Nutritive Value of Pentosan (IX).

Distribution of Hardly Soluble Carbohydrates.

(pp. 315～324)

By Hisayoshi Iwata and Ryosuke Kikuchi.

(Morioka Imperial College of Agriculture and Forestry;
Received December 4, 1941.)

The distribution of pentosan and crude fiber in the uncultivated vegetable food materials, ordinary food materials, herbaceous plant materials and ordinary stuffs in North Japan were investigated.
